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Procedia Chemistry 8 (2013) 175 – 184

Procedia Chemistry

Youth in the Conservation of Cultural Heritage, YOCOCU 2012

Characterization and weathering of motion-picture films with support of cellulose nitrate, cellulose acetate and polyester

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Abstract

The microanalytical characterization of several motion-picture film samples of different support layers (cellulose nitrate, cellulose acetate and polyester) is presented. The goal of the work is to provide, by performing analyses and collecting data, a clear picture in order to better define the nature of the samples, their morphology, and any forms of degradation, by focusing on the causes and the mechanisms of weathering. To achieve these purposes several microanalitical techniques were used.

Selection and peer-review under responsibility of the IA-CS (Italian Association of Conservation Scientists) and University of Antwerp

Keywords: characterization; motion-picture film; weathering; XPS; SEM

1. Introduction

In the last years cinema technicians, scientists and restorers have felt pressing and urgent the need to create the right conditions for the conservation of motion-picture films that require special care and precautions in order to prevent, or better, slow down the weathering deterioration. Since the birth of photography, many substances and methods have been used for the productions of motion-picture films. Some materials were extremely unstable, others very sensitive to the physical contact and almost all were - and still are - sensitive to environmental factors, not only to the temperature, relative humidity, air pollution, but also to substances which may come from

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Selection and peer-review under responsibility of the IA-CS (Italian Association of Conservation Scientists) and University of Antwerp
doi:10.1016/j.proche.2013.03.023

objects placed in contact with them [1-4]. There are some papers reporting the guidelines for operating inside of a motion-picture archive, the optimal conditions of environmental temperature and humidity to achieve, the materials to be used in storage and safety precautions for handling these particular types of documents [5-7]. The knowledge of the substances used during the preparation of motion-picture films is crucial in the development of techniques and methodologies that can prevent their degradation. The diagnostic characterization is therefore essential to implement conservation strategies to avoid that time alters the photographic films, forbidding their deliver to the future. In this work the micro-analytical characterization of several motion-picture film samples of different kinds, having the support in cellulose nitrate, cellulose acetate and polyester, is presented. The work provides a clear picture of the performed analyses and of the collected data in order to define the nature of the samples, their morphology, and any forms of degradation, by focussing on the causes and the mechanisms of weathering. In order to achieve these purposes we used several microanalitical techniques such as XPS (X-ray photoelectron spectroscopy), which allows to obtain information on surface composition of the samples, Scanning Electron Microscopy (SEM) coupled with the probe microanalysis EDX (energy dispersive X-ray), which allow the observation of morphological structure and to analyze the elements that characterize different areas of the samples. Other observations were accomplished by the aid of Optical Microscopy (OM), Gas Chromatography coupled with Mass Spectrometry (GC-MS/SPME) and, finally, the FT-IR (Fourier transform infrared spectroscopy) was performed to identify the composition of the layers of the different film samples.

1.1. Historical aspects

In order to better understand what the photographic film represents, it is important and fundamental a brief history of photography, its "inventors" and the chemical processes involved. Its birth is related to discoveries and observations made in a very broad span of time. In the table 1 the most important steps in the history of photography are highlighted.

When	Who	What
1802	Thomas Wedgwood	Leather and silver nitrate
1816	J. Nicephore Niepce	Heliography
1835	**Jaques Daguerre**	**Daguerreotype**
1835	**Fox Talbot**	**Calotype**
1851	**Frederick Scott Archer**	**Wet Collodion**
1871	Richard Maddox	Emulsion into gelatin
1888	George Eastman	Camera Kodak n°1
1889	Thomas Edison	Substrate in nitrocellulose; motion-picture film
1895	Lumière brothers	First cinematographic projection
1908	Kodak	Substrate in cellulose acetate
1948	Kodak	Introdution of the acetate for motion-picture films
1960	Kodak	Kodak Estar, polyester film

Table. 1. The most important step of the history of photography

In particular, the schemes of the daguerretype, the calotype and the wet collodion processes are shown in fig.1

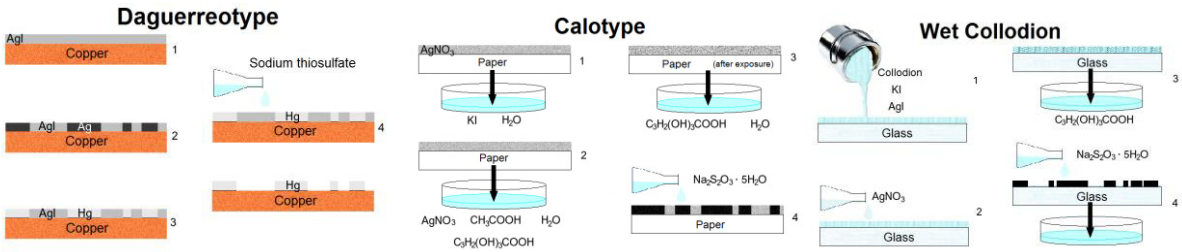

Fig. 1. (a) Daguerreotype process; (b) calotype process; (c) wet collodion process

1.2. Chemical aspects

The photographic technique is based on a chemical process, whose main component is silver. This is introduced in the form of salts, the silver halides: AgBr (silver bromide), AgCl (silver chloride), AgI (silver iodide). When the light radiation strikes the silver halides, the anions X^{-1} is oxidized to X^{0}. The electron is captured by the Ag^{+1} that is reduced to Ag^{0} metal. These reactions lead to the formation of so-called "latent image", not visible since it consists of a small number of atoms of silver. The latent image is made visible through the "development“ step which consists in a chemical reduction of the exposed silver halides to metallic silver by using phenol, a hydroquinone. The following step is the fixing that eliminates the silver halides residues by using sodium thiosulphate. When the fixing process is finished, negative image has been obtained. If the images are projected, as in our case, it is necessary to implement the process of "inversion" in order to obtain positive images directly from the negative. In the process of inversion the b/w film is submitted to a second development in a bath containing methyl para aminophenol sulphate, hydroquinone and sodium carbonate and is then washed with running water. The following step is the whitening, in which the film undergoes to the combined action of sulphuric acid and potassium dichromate until the images formed by silver (black) become white. After a further washing, the following step is the “brightening” through which areas of strong brightness of the image must correspond to a total transparency of the film; the substances used are sodium thiosulphate and anhydrous sodium sulphite.

1.3. Layers of the motion picture films

The films are composed of several layers, each with different characteristics and properties. The most important are the support, the emulsion, the antihalo and the protective layer. The emulsion layer is constituted by animal gelatine which contains the silver halide, light-sensitive compounds that allow the formation of the image. The animal gelatine was chosen in the photographic field thanks to the gel-sol characteristic properties and, moreover, for its incapability of reacting with halides, allowing the stability of the entire film. Several materials have been used for the support layer [5-7]. At beginning, cellulose nitrate was used; however, its application in the field of cinematography was not appropriate, due to the high flammability of the material arising from the processes of autocatalytic degradation due to the production of NOx that develop from the support in the presence of moisture. In 1948, cellulose nitrate was replaced from the more stable cellulose acetate and the films were named "safety film". The support of cellulose acetate proved, also, to be not very suitable: in fact, due to the action of temperature and humidity, the cellulose acetate frees acetic acid which gives rise to the smell of vinegar typical of the “vinegar syndrome”. Because of the instability of these products based on cellulose, since 1960 polyester supports have been introduced and are still used [8-9]. The polyesters are a class of synthetic polymers obtained by polymerization processes. In our field of interest polyethylene terephthalate, indicated with the

acronym PET has been employed. The films are equipped with an anti-halo layer that can be applied between gelatine and support or in the back of the support itself and its role is to absorb the reflections, by avoiding noise for the images. Finally the protective layer, localized at the top of the film, prevents the deposition of dust on the gelatine layer and has the function of preventing scratches that can cause disturbances to the images.

2. Experimental data

2.1. Sampling

The study was accomplished on samples with different types of support (cellulose nitrate, cellulose triacetate and polyester), supplied from the Foundation of *Centro Sperimentale di Cinematografia (CSC), Cineteca Nazionale, Rome*, "Spadaro" and "Margherita" cinema theaters in Acireale (CT) and the society SAC, Catania. The samples coming from Rome were mailed inside a box hermetically sealed. The samples analyzed, the type of support and the source are summarized in the table 2.

Sample	Codex	Type of support	Source
	**R1**	cellulose nitrate	CSC, Roma
	**A1**	cellulose triacetate	Multisala Margherita, Acireale
	**A12**	cellulose triacetate	CSC, Roma
	**A5**	cellulose triacetate	CSC, Roma
	**A14**	cellulose triacetate	CSC, Roma
	**2E**	Polyester	Cinema Spadaro, Acireale
	**R2**	Polyester	CSC, Roma

Table 2. Samples analyzed during the work

Moreover, other samples were collected (showing variable degradation from 0 to 100 %) and analyzed in order to have much more informations regarding the condition of the films.

2.2 Instrumental measurements

The microstructure and the composition of the different samples were investigated using analytical methods such as Optical Microscopy (OM), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray analysis (EDX), Fourier Transformed Infrared spectroscopy (FTIR) and X ray Photoelectron Spectroscopy (XPS). Samples were imaged using a VP LEO 1550 SEM instrument with a field emission source and a controlled electron energy of 15 keV. The samples in many cases did not require any metal coating. The SEM system was equipped with EDX microanalysis. The microstructure was investigated using a Bruker-AXS D5005 XRD instrument. Infrared spectra of the powdered samples were recorded on a JASCO FTIR, collecting the spectra with 80 scans at 4 cm-1. Gas Chromatography coupled with mass spectrometry Solid-Phase Micro-Extraction (GC-MS SPME) measurements were accomplished by using Perkin Elmer and Agilent 6890 instruments. XPS measurements were performed on PHI 5600 system using a X-ray Al-Kα standard source (hν =1486.6 eV). The energy scale of the spectrometer was calibrated with reference to the Ag 3d3⁄2 = 368.3 eV photoelectron line. Binding energies were calculated with respect to the C 1s ionization at 285.00 eV from adventitious carbon that is generally accepted to be independent of the chemical state of the sample under investigation

3. Result and discussion

3. 1 Cellulose Nitrate support sample

3.1.1 R1 Sample

The R1 film dates back 1915 and was collected from the reef of the movie "…e salverai l'onore!" of Giuseppe Giusti. The film, having nitrate cellulose as support, appears brittle, in some points damaged, and, moreover, some cracks are visible (fig.2a). In particular, the reel emanates a strong, pungent and bad smell due to the deterioration of the support and the emulsion of the film [10-12]. By observing the reef,, it is possible to observe the low thick of the photosensitive emulsion layer that, in some points, is absolutely absent, by showing the underlying layer (support). The visible injuries have produced an irreversible loss of material and, probably, the weathering comes from the unsuitable conservation conditions (relative humidity and temperature variations created contractions and expansion of the texture of the film, determining a high level of mechanical stress, determining the weakness of the structure of the reel). In particular, the OM and SEM cross section analyses of sample R1 show the different layers of the film(fig.2b): the emulsion layer (lower layer), the cellulose nitrate support (intermediate layer) and the anti-halo layer (upper layer).

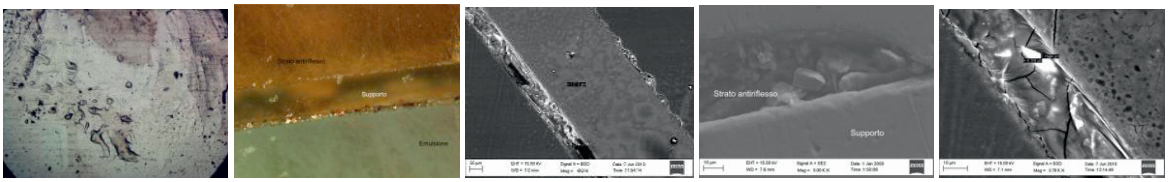

Fig. 2. (a) R1 sample damages; (b) OM image of the different layer of R1 sample; (c) SEM image of the different layer of R1 sample; (d) SEM image of silver particles in the emulsion layer; (e) SEM image of fractures in emulsion layer

The photosensitive emulsion layer appears as single and transparent, there are some dark patches due to the presence of silver grains (fig.2c). The upper layer presents very thin, discontinuous, transparent, non-homogeneous over the whole surface. Some photosensitive silver particles (fig.2d), diamond-shaped, having the width of about 6μm and the length of about 16,5 μm, are present in the emulsion, as evidenced by SEM/EDX measurements. Through these analyses, the thickness of each layer was determined and the values are reported in the table 3. The figure 2e, moreover, shows the fractures (having thicknesses of about 1 micrometer) in the emulsion layer. Most of the lesions are perpendicular to the axis of the support and are due to mechanical stress of the different layers involved. XPS spectra were acquired in the area where the gelatin layer was present.

Description	**thickness**
Film	177.5 μm
Substrate	141 μm
Emulsion	28 μm
Anti-halo layer	8.5 μm

Table3: thickness of the layers in the R1sample

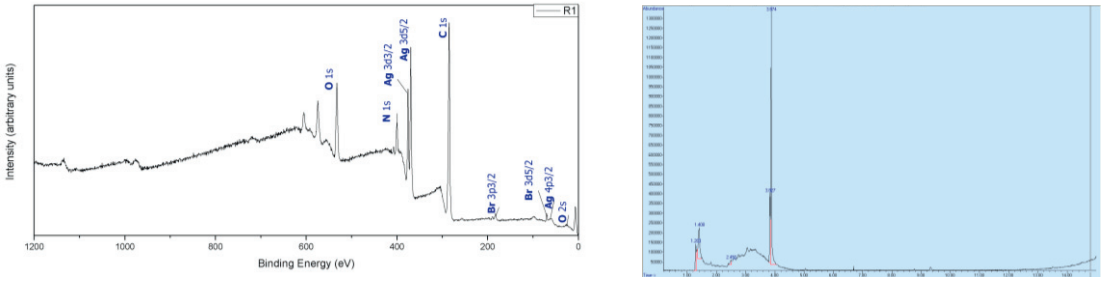

Fig. 3. (a) XPS survey spectrum of emulsion layer; (b) GC-MS/SPME spectrum for R1 sample

The survey spectrum of the sample where the gelatin is visibly present shows the presence of the peaks relating to the silver, nitrogen, oxygen, bromine and carbon ionizations (fig.3a). Despite the acquisition of the spectrum survey was carried out in a white area of the film, silver and bromine were found. It is possible that the presence of these elements is due to a bad fixing process, usually accomplished in order to take off the AgBr in the regions not exposed to light. With regard to the XPS spectrum relative to the ionization of the carbon 1s, it is possible to observe, after the process of deconvolution, the presence of the peak attributable to the carbon bonded to the oxygen in the peptide structure of the gelatin. The ionization of the nitrogen 1s shows a peak at 407.3 eV

attributable to the group NO_2 of cellulose nitrate support and a very intense peak at 399.8 eV due to the gelatin of the emulsion layer. The oxygen 1s peak at 532.0 eV is attributable to the NO_2 group of the cellulose nitrate. It is possible that the thickness of gelatin in the region analyzed is thin enough to allow detection of the composition of the underlaying support. The spectrum relating to the ionization of the bromine 3d shows the peak $3d_{5/2}$ at an energy of 69.1 eV attributable to bromide ions. Silver ionization spectrum shows peaks related to orbital $3d_{5/2}$ and $3d_{3/2}$. The deconvolution of the peak of the Ag $3d_{5/2}$ shows the presence of two peaks at different energy: the first energy of 368.4 eV attributable to silver alloy to bromine. GC-MS/SPME technique was also used for R1 sample and the spectrum is reportedin figure. This technique has shown the presence of camphor used in the preparation of cellulose nitrate support, obtained my mixing nitrocellulose with about 11% of nitrogen, camphor and alcohol.

3. 2 Cellulose triacetate support samples

3.2.1 A1 sample

The A1 sample was collected from a 35mm color reel, having the mark “Safety Film”, indicating that the support is constituted from cellulose acetate material. The film is in fairly good condition, even if it presents numerous abrasions visible onto the emulsion surface. The OM/SEM cross section images show the different layers present in the film (fig.4a and fig.4b). It is possible to observe three coloured layers (yellow, ciano, magenta) onto the emulsion layer surface, revealing that the film is coloured.

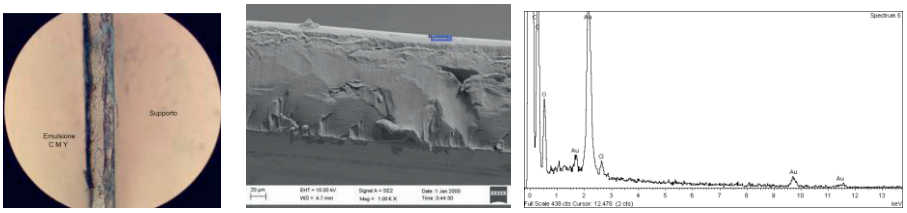

Fig. 4. (a) OM image of the different layer of A1 sample; (b) SEM image of the different layer of A1 sample; (c) EDX of emulsion layer

The thickness of the film is around 180μm while the thickness of the photosensitive emulsion layer is around 20 μm and appears to be constant in all the film. EDX spectrum (fig4.c), acquired in the emulsion layer, allowed to identify the presence of silver chloride, due to the light-sensitive compound used during the preparation phase, even if in the literature it is found that the halide used in the emulsion is mainly AgBr, preferred to the chloride for the lower required times of exposure .

3.2.2 A12 sample

The A12 sample was collected from a colored, degraded and fragile motion-picture film (fig.5a). The surface of A12 sample is sticky (the reel is glued on itself) and many bubbles are visible between the emulsion and support (it is not possible to distinguish the boundary of separation between this two layers). A persistent smell of vinegar is felt and, moreover, the surface and the edges of the film are extremely curled. The deterioration caused the total loss of the images and the film is extremely fragile. The reasons of the alterations are to be searched in the process of weathering due to the time and to the not properly controlled storage conditions [13-15]. SEM image shows that the thick of the film is about 166 microns and the presence in the emulsion layer of some grains of silver, generally of small size and irregular shapes and scattered throughout the layer (fig.5b).

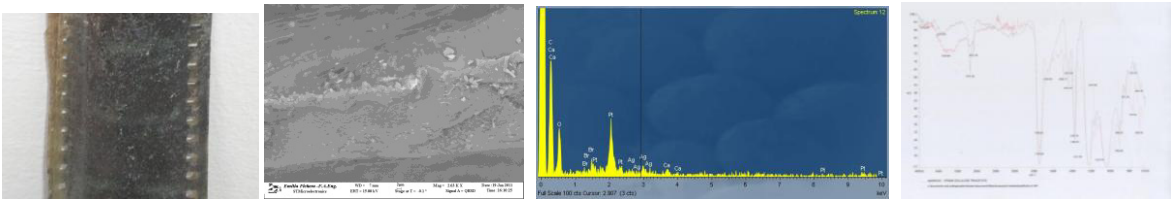

Fig. 5. (a) A12 sample photo; (b) SEM image of the emulsion layer of A12 sample; (c) EDX spectrum of silver grains; (d) FTIR spectra overlapping

EDX analyses were performed onto the grains of silver and the spectrum (fig. 5c) reports the presence of the peaks relative to silver and bromine. The bromine is used in the preparation phase in order to make possible the formation of the image and, usually, it is taken off with the fixing process. Its presence in the sample A12 is probably due to a not perfectly execution of the fixing treatment. FT-IR analyses were accomplished in an area where the emulsion was present. Figure shows the overlapping of the spectrum relating to the analyzed sample and the spectrum of the standard cellulose triacetate. By comparing the standard spectrum of cellulose triacetate with the emulsion layer spectrum (fig.5d), it can be observed that there is overlapping of the peaks at 3428, 2921, 1738, 1435, 1367, 1212, 1165, 1050, 900, 832, 690 cm^{-1}, confirming that the support of the film A12 is constituted of cellulose triacetate. The most characteristic feature is the absorption band falling at around 1735 cm^{-1} which can be attributed to the stretching vibrations of the carbonyl group. The bands at 1212 and 1050 cm^{-1} correspond to the stretching vibrations of C-O bonds. The band at 2921 cm^{-1} is attributable to the CH bonds and broadband centred at 3428 cm^{-1} is attributed to the stretching vibrations of O-H bonds[14]. The peaks 1646, 1540, 1488, 755 cm^{-1} are not belong to the standard spectrum of triacetate and are related to the amino group of amino acids present in the gelatine. In fact, the large band centred at 3428 $cm^{-}1$ may be due to stretching -NH of the secondary amide while the peak at 1646 cm^{-1} refers to the stretching of C = O group and the peaks at 1540 and 1488 cm^{-1} refer to the bending NH [15].

3.2.3 A5 sample

The A5 sample was collected from a color and partially degraded motion-picture film. The images in the film are markedly faded (fig. 6a). SEM images let to distinguish the support and the emulsion layers and, moreover, are visible silver grains distributed within the emulsion, in higher amount and with more regular shapes, if compared to the sample A12 (fig. 6b).

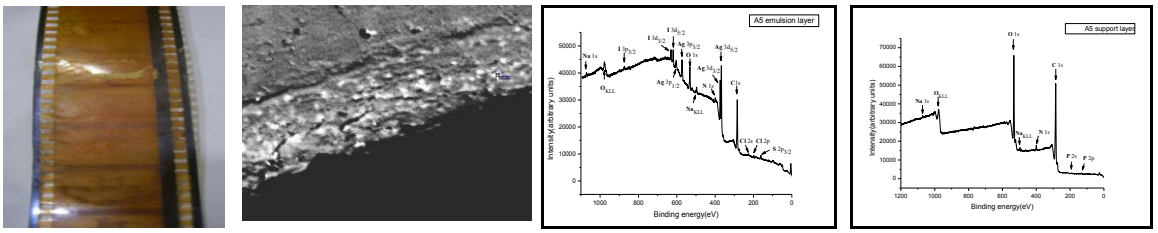

Fig. 6. (a) A5 sample photo; (b) SEM image of the emulsion layer of A5 sample; (c) XPS spectrum of emulsion layer; (d) XPS spectrum of support layer

XPS measurements, in survey and in multi modes, were accomplished in order to determine the elemental composition and the chemical state oxidation of the elements identified. The survey spectra acquired in the area of the emulsion and the support area are reported in the fig. 6c and fig. 6d.

By regarding the emulsion layer, the deconvolution of silver peak showed the presence of Ag^{+1} and the deconvolution of sulphur peak showed the presence of S^{-2}, indicating that Ag_2S is present, coming the following reaction that occurs, in the presence of humidity, between silver metal and H_2S in the atmosphere:

$2Ag + H_2S + O_2 \rightarrow Ag_2S + H_2O$

The presence of iodine and chlorine was also observed while the bromine was absent. Low intensity peak relative to phosphorus was also present in the support layer: it probably is relative to triphenyl phosphate compound, plasticizer added during the manufacturing phase for improving the resistance to moisture and decrease the risk and speed of combustion.

3.2.4 A14 sample

The A14 sample comes from a black and white motion-picture film in visibly good conditions (fig. 7a). The SEM images of the sample (fig. 7b) show that the thickness of the film is about 122 μm, while the emulsion layer thickness is about 4μm, smaller if compared to the thickness of the other films containing cellulose acetate. This fact can be explained by assuming that the film was produced later than the film relative to the sample A5 and that a technique able to reduce the thickness of the layers was used to prepare it. The EDX spectra acquired for emulsion layer show only the presence of silver.

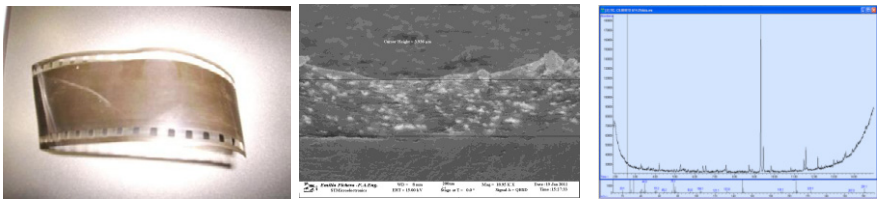

Fig. 7. (a) A14 sample photo; (b) SEM image of the different layers of A14 sample; (c) GC-MS/SPME spectrum for A14 sample

GC-MS/SPME was also used for analyzing this sample (fig.7c). Through this technique, the presence of nitrostyrene and hydroxychinolin was observed. It is possible the nitrostyrene compounds were added during the preparation of the film in order to have a better adhesion between the emulsion and the support layers . As reported in the literature, the hydroxychinolin could be added to the gelatine in order to improve the hardening properties of the emulsion layer.

3. 3 Polyester support samples

3.3.1 2E and R2 samples

The 2E sample comes from 35mm color movie film entitled "The Ring 2" (2005) by Hideo Nakata. It appears in excellent condition (abrasions or lesions are not visible on the sample). The R2 sample was collected from a 35mm black and white movie film of a recent production trailer. The two films are shown together because both samples are of modern manufacture and in excellent conditions. The OM/SEM images of the sample 2E show the presence of the different layers: the transparent polyester support, the photosensitive emulsion layer, the double layer formed of gelatine and colored in yellow, magenta and cyan, while the OM/SEM images of the sample R2 shows two layers: the photosensitive emulsion layer and the state anti-reflection (it is a black and white film). The SEM images highlighted that the thickness of the film and of the emulsion layer are respectively about 128.7 μm and 6.0 μm. The emulsion layer contains the photosensitive particles, whose dimensions range between 325 nm and 398 nm (in effect, they are particle agglomerates). By comparing the emulsion layer of these samples with the emulsion layer of the film having the cellulose acetate support, It is possible to observe the high amount of silver particles, having uniform size. The EDX measurements, performed

in several points of the emulsion layer, reveals the presence of silver and bromine . The presence of bromine is probably due to a bad fixing treatment of the film. The XPS "survey" spectrum of the emulsion layer of R2 sample is reported in fig. 8d)

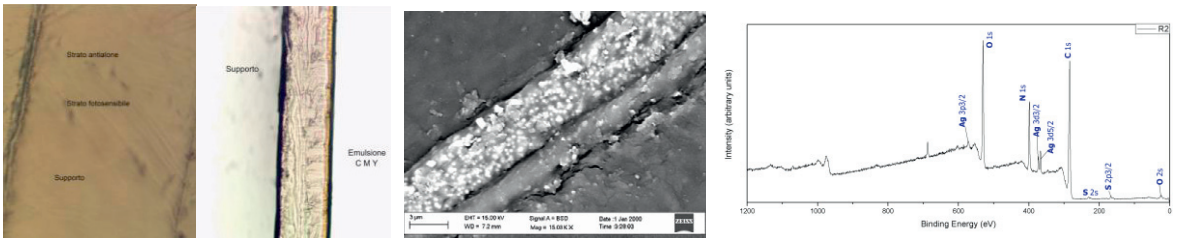

Fig. 8. (a) 2E sample photo; (b) R2 sample photo; (c) SEM image of the different layers of R2 sample; (d) XPS spectrum of emulsion layer

The presence of sulfur peak underlines that in the emulsion layer of this motion-picture film is present Ag_2S compound, although the condition of the film are still good.

Acknowledgements

The authors wish to thank the "Centro Sperimentale di Cinematografia (CSC)" in Rome and, in particular, Dott. Marco Bernardini and Dott. Mario Musumeci.

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